Studies on the Determination of Metals by Extraction Method of Metal Organic Compound. V : Determinations of Copper and Bismuth with Sodium Diethyldithiocarbamate

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Determinations of Copper and Bismuth with Sodium Diethyldithiocarbamate*

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Synopsis

The salt of copper and bismuth by sodium diethyldithiocarbamate were extracted completely with organic solvents and gave clear extracts, and its absorbancy was measured by the Beckman Model DU spectrophotometer to determine the amount of copper and bismuth.

The organic solvents used were amyl acetate, carbon tetrachloride, benzene, toluene, xylene, chloroform, and amyl alcohol, of which a mixed solvent of amyl alcohol and ethyl acetate in the ratio 3 : 1 was found to be the best one for the extraction. The minimum determinable amount of copper was 1γ at the wave-length 440 mμ and that of bismuth was 10γ at 370 mμ, that is, the molecular extinction coefficient calculated for copper and bismuth in carbon tetrachloride were 16637 and 14296, respectively. By applying this method to the determination of copper in lead alloys, so small a content as 0.0002 per cent was successfully determined.

I. Introduction

Numerous investigations have already been reported(1) as to the determination of copper with sodium diethyldithiocarbamate, most of which are based on the colorimetry of this complex salt extracted with carbon tetrachloride. Willmott and Raymond used ether for the extraction in determining copper in lead and lead alloys and carried out colorimetric measurement with Spekker absorptiometer.

There was virtually no detailed report on the extraction with other organic solvents, and so the present auther carried out a comparative examination of various organic solvents in order to obtain an effective solvent. Y. Murakami added hydroxylamine prior to the extraction with carbon tetrachloride in order to make the extraction with organic solvent complete, as a modification of the colorimetric determination of copper with sodium diethyldithiocarbamate. The present auther found that the isolation was complete when extracted from

* The 757th report of the Research Institute for Iron, Steel and Other Metals.

(1) T. Callan and J. Henderson, Analyst, **54** (1929), 650.
L. W. Conn, A.H. Johnson, H. A. Trebler, and V. Karpenko, Ind. Eng. Chem., Anal. Ed., **7** (1935), 15.
T. P. Hoar, Analyst, **62** (1937), 657.
F. Ensalin, Metall u. Erz., **38** (1941), 78.
T. C. J. Ovenston and C. A. Parker, Anal. Chim. Acta, **4** (1950), 135.
P. L. Willmott and F. J. Raymond, Analyst, **25** (1950), 24.
R. L. Lacoste, M. H. Earling, and S. E. Wiberley, Anal. Chem., **23** (1951), 871.
Yukio Murakami, Bull. Chem. Soc. Japan, **23** (1950,) 3.

ammonia-alkaline medium in the presence of ammonium citrate, ammonium sulfate, or ammonium tartrate but that the isolation was difficult in the absence of these ammonium salts and reproducibility was not good. For the utilization of this method to the determination of copper in metals, the determination of bismuth, which interferes with the microdetermination of copper in lead metal by extraction with carbon tetrachloride, was carried out and the permissible amount of bismuth was studied. The present paper describes the results thereby obtained.

II. Experimental results

(1) Reagents and apparatus

Reagents: Standard copper solution (10 γ/ml) was prepared from Merck's $CuSO_4 \cdot 5H_2O$, standard bismuth solution (40 γ/ml) was prepared from 'guarranteed $Bi(NO_3)_2$, ammonium citrate solution (10 per cent aqueous solution), and other reagents used were the same as those described in Part III of this series[2].

Apparatus: Beckman Model DU spectrophotometer (1-cm cell) was used.

(2) Method of measurement

To the solution of metal, 10 ml of 10 per cent ammonium citrate solution and 2 ml of 0.1 per cent sodium diethyldithiocarbamate solution were added, rendered to alkaline with ammonium hydroxide and extracted with 5ml of organic solvent. The transmittancy of the extract solution was measured, absorbancy curve was plotted, and the amount of the metal was obtained by the measurement of absorbancy at a suitable wave-length.

1. Copper

(1) Absorbancy curve

To the copper solution were added 10 ml of 10 per cent ammonium citrate solution and 2 ml of 0.1 per cent sodium diethyldithiocarbamate solution, and the mixture was rendered to alkaline with ammonium hydroxide 5 ml of amyl alcohol added, and shaken vigorously for one minute. When the mixture separated into two layers, the organic solvent was transferred to the 1-cm cell, transmittancy measred at wavelength 320-1000 mμ, and absorbancy curve was plotted, as shown in Fig. 1. Amyl alcohol was measured as a

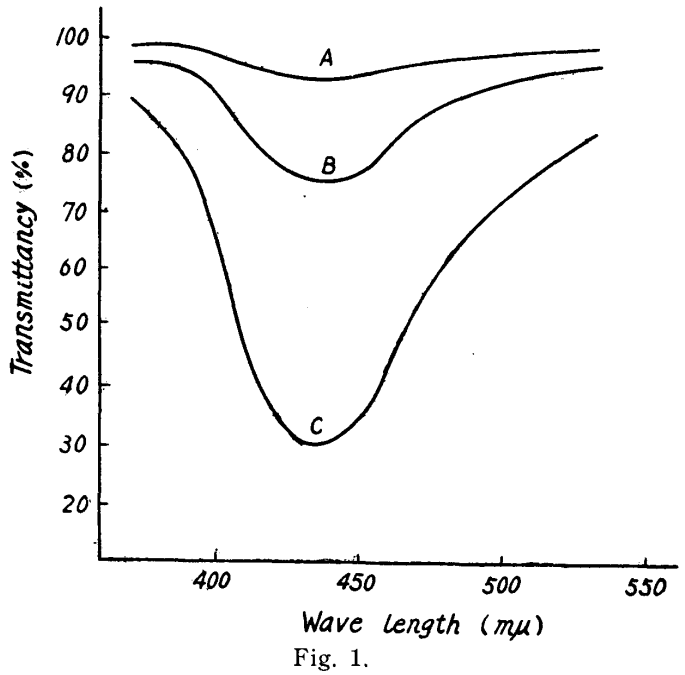

Fig. 1.

(2) E. Sudô, Sci. Rep. RITU, 746th (1954); J. Chem. Soc. Japan **73** (1952) 626.

standard, and in Fig. 1 A, shows the absorption of the reagent alone, B, 5γ of copper, and D, 10γ of copper. As can be seen from Fig. 1, the most suitable wave-length is at 440 mμ. It was found that the minimum amount of sodium diethyldithiocarbamate necessary for the coloration was 1 ml of 0.1 per cent solution for 5γ of copper.

(2) Range of pH of the solution for extraction

Extraction could be effected approximately from pH 1 to 12 of ammonia-alkalinity, and was not complete outside this range. In the determination in ammonia-alkaline solution, the presence of ammonium citrate or sulfate makes the separation of the solvent easy in extraction, while the absence of such a salt makes it difficult to separate the two lyers and reproducibility was not good. From the examination of the effect of the amount of such salt present it was seen that a good result could be obtained in the case of over 1 ml of 10 per cent ammonium citrate solution in a total amount of the solution of 25 ml. Below this amount, the aqueous layer refused to become clear and the values of measurement tended to come out lower.

(3) On the solvents

The degrees of extraction of various solvents were compared with each other and the results obtained are shown in Fig. 2. The best result is obtained with a mixed solvent (3 : 1) of amyl alcohol and ethyl acetate, while carbon tetrachloride, benzene, toluene, xylene and chloroform showed similar absorption.

(4) Relationship between the amount of metal and extinctancy

A curve was plotted with various amounts of metal in ammonia-alkaline solution, from which it was found that the amount of metal and extinctancy are in linear relation, and that a definite amount is reached in the range of 1–15γ of copper.

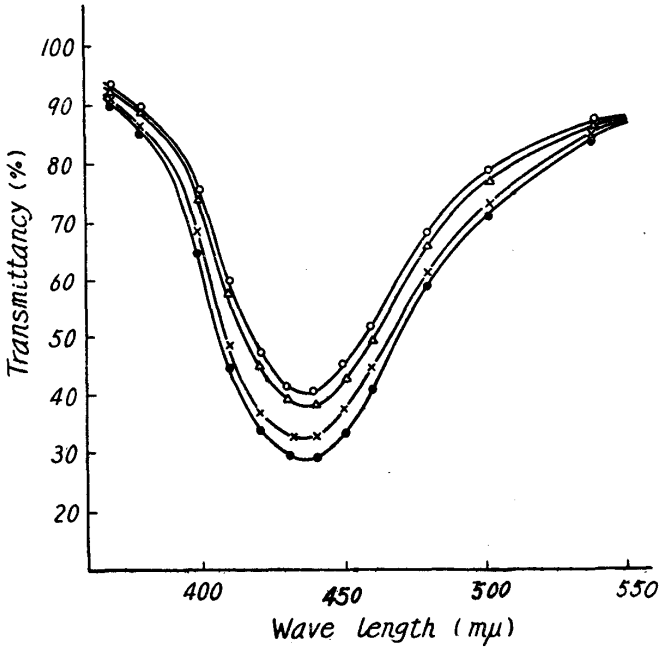

Fig. 2.

-○- Amyl acetate
-△- Carbon tetrachloride, benzene, toluene, xylene, chloroform
-×- Amyl alcohol
-●- Amyl alcohol : ethyl acetate (3 : 1)

2. Bismuth

(1) Suitable wave-length for determination and relation between the amount of metal and extinctancy

Bismuth, similar to copper, forms colored complex salt with sodium diethyldithiocarbamate and this complex can be extracted with organic solvents. The absorption curve of this extract, as given in Fig. 3, shows the maximum absorption

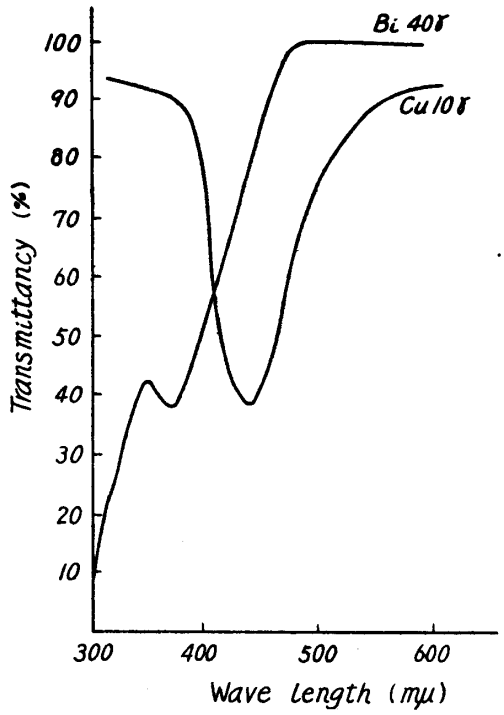

Fig. 3.

at 370 mμ molecular Extinction coefficient is 10450 when extracted with carbon tetrachloride. Determinable amount of bismuth at this wave-length showed a linear relation with extinctancy of extract, and determination of bismuth could be effected in the range of 10-100 γ.

3. Determination of copper in lead metal

The present method was applied to the determination of copper in lead metal.

(1) Effect of bismuth

The element which might interfere in such a determination, would be bismuth, as iron can be eliminated as a complex by adding ammonium citrate. The effect of bismuth interference was, therefore, examined.

The complex salt of various amounts of bismuth and of 10γ of copper was extracted with carbon tetrachloride this solvent was the best one for extraction and cheap and the extinctancy was measured at the wave-length 440 mμ, suited to the determination of copper, and at 370 mμ, suited to the determination of bismuth. The results are shown in Table 1, from which it can be seen that the effect of bismuth is nil for the determination of 10γ of copper up to 50γ of bismuth.

Table 1.

Amount of bismuth added to 10γ Copper (γ)	Extinctancy	
	at 440 mμ	at 370 mμ
0	0.450	0.000
10	0.448	*0.150
20	0.450	*0.230
40	0.450	0.415
50	0.451	0.530
60	*0.470	0.620
70	*0.480	0.745

* Higher values due to interference

Above that amount, the presence of more bismuth tends to give high values so that bismuth should be separated if presented above 50γ. As shown in Table 2, the permissible amount of copper is 5γ for 10γ of bismuth and is 10γ for 30γ of bismuth. In other words, when bismuth and copper are present respectivly within 30γ and 10γ, they can be determind at 440 mμ for copper and 370 mμ for bismuth and above that amount, copper should be eliminated as a complex salt with potassium cyanide and the coloration of bismuth alone allowed to develop.

Table 2.

Amount of copper added to 10γ of bismuth (γ)	Extinctancy	
	at 440 mμ	at 370 mμ
0	0.000	0.100
5	0.212	0.100
8	0.352	*0.145
10	0.450	*0.152

* Higher values due to interference

(2) Procedure

Ten gram of the sample is dissolved in 60 ml of nitric acid (1 : 4), evaporated to dryness, and tin and antimony are separated. Sulfuric acid is added to this residue, diluted with about 10 volumes of water, and filtered into a 250 ml flask. A suitable amount of this solution (corresponding to 1-10γ of copper) is placed in a separatory funnel, 10 ml of 10 per cent ammonium citrate solution was added, and rendered to alkaline with ammonium hydronide. To this solution are added 2 ml of 0.1 per cent sodium diethyldithiocarbamate solution and 5 ml of carbon tetrachloride, shaken vigorously for one minute, and allowed to separate into two layers. The organic solvent layer is transferred to the 1 cm cell and its extinctency is measured at 440 mμ. The results of analysis on synthetic samples by this method are shown in Table 3, from which it can be seen that 0.0002 per cent of copper can be determined accurately.

Table 3.

Amount of copper added to Pure Lead (%)	Amount of Copper found (%)
0.0150	0.0153
0.0120	0.0120
0.0100	0.0100
0.0050	0.0050
0.0030	0.0030
0.0010	0.0010
0.0002	0.0002

Conclusion

(1) Diethyldithiocarbamate complex salt of copper and bismuth was extracted with an organic solvent and its absorbancy curve was obtained by the Beckman model DU spectrophotometer.

(2) The most suitable wave-length for determination was found to be 440 mμ for copper and 370 mμ for bismuth. The amount of metal and extinctancy were in linear relation in both cases, and the minimum amount determinable was 1γ of copper and 10γ of bismuth.

(3) The range of pH of solution suitable for extraction was from pH 1 to ammonia-alkaline range. The presence of ammonium citrate was found to be necessary in extracting from ammonia-alkaline solution. No great difference was

found in various extraction solvents but the best result was obtained with a mixed solvent of amyl alcohol and ethyl acetate in the ratio of 3 : 1.

(4) The present method was applied to the determination of copper in lead metal, in which 0.0002 per cent of copper was accurately determined.

Acknowledgement

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